
(12) UK Patent Application (19) GB (11) 2 101 596 A

- (21) Application No 8217898
(22) Date of filing 21 Jun 1982
(30) Priority data
(31) 8121710
(32) 14 Jul 1981
(33) United Kingdom (GB)
(43) Application published
19 Jan 1983
(51) INT CL³
C07C 21/06 17/154 B01J
23/84 C07C 19/045
21/073
(52) Domestic classification
C2C 200 20Y 313 31Y
339 410 413 414 418 419
440 444 44Y 468 469
47X 561 562 567 65Y
73Y EH HA
B1E 1147 1180 1298
1317 1331 1351 1363
1364 1381 1441 1461
1492 1500 1513 1631
1701 1702 1714 1721
1738 1743 AD
U1S 1514 B1E C2C
(56) Documents cited
GB 1016495
GB 0969937
(58) Field of search
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B1E
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- (54) Oxychlorination of alkanes to monochlorinated olefins
(57) A process for the production of a monochlorinated olefin comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium, and is useful for the production of vinyl chloride from ethane.

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SPECIFICATION
Production of monochlorinated compounds

The present process relates to the production of monochlorinated compounds by the oxychlorination of alkanes.

5 Vinyl chloride is at present manufactured in an essentially two stage process by the oxychlorination of ethylene. Since ethane is potentially a much cheaper feedstock there is considerable incentive to devise a suitable alternative process, particularly if a single stage process can be developed. Several possible processes have been disclosed (e.g. US 3,937,744; Ger Off 2,540,067; US 3,629,351 and GB 2009164). In general these employ similar catalysts to those employed for ethylene oxychlorination, but it is generally found that much higher reaction temperatures are required (450—700°C as compared with about 350°—500°C). This is a serious disadvantage since the catalyst can be molten or partially volatile (necessitating a complex reactor design) and the highly corrosive reaction conditions require the use of expensive construction materials.

10 We have now discovered certain catalysts which can operate in a temperature region substantially below that hitherto possible and thus reduce corrosion/erosion problems. The catalysts may be used in the solid particulate state, thus avoiding reactor problems associated with molten salts and permitting the use of both fixed and fluid bed reactors. These catalysts thus afford the advantage of a selective single stage process based on ethane feedstock.

15 According to the present invention, we provide a process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium.

20 The catalyst composition may include one or more additional components, for example, cerium, thorium, iron or zinc compounds.

25 The process of the invention is applicable to a range of alkane starting materials, especially alkanes having 2 to 4 carbon atoms, for example ethane. The starting material may comprise an alkane/alkene mixture. The alkene may be, for example, ethylene, propylene and various butenes.

30 The process of the invention is especially applicable to the production of vinyl chloride from ethane or ethane/ethylene mixture.

35 Suitable catalyst compositions include those in which the atomic ratio of copper:manganese:titanium is in the range 1:0.1:1 to 1:10:25. Particularly valuable results are obtained when this ratio is substantially 1:1:10.

40 When additional components are present, the atomic ratio of each additional metal relative to the copper present is suitably within the range 0.1 to 5. Particularly valuable results have been obtained when the atomic ratio Cu:Mn:X:Y:Ti is substantially 1:1:0.5:0.5:10, the metals X and Y being selected from Ce, Th, Fe and Zn.

45 The catalyst may conveniently be prepared by coprecipitation of the appropriate oxides, which coprecipitation may be effected chemically, thermally or electrically, or by a combination of these methods. Suitably, the coprecipitation comprises preparing a solution containing the materials from which the desired components can be precipitated. Alternatively, the catalysts may be prepared by sintering the components or by combining the molten components. Under reaction conditions, the oxides may be converted partly or wholly to the corresponding chlorides and/or oxychlorides.

50 The catalyst may be supported if desired on known carriers such as, for example, silica, alumina, titania or silicon carbide. The surface area of the support can be varied widely but is usually in the range 0.1 to 50 m²/g.

55 The supported catalyst may be employed in fixed, moving or fluidised beds of the appropriate size.

60 The reaction temperature may vary according to the reactant employed. Suitably, for example for the oxychlorination of ethane or ethane/ethylene, the reaction temperatures are in the range 250°C—500°C, for example 300°C—475°C. The reaction is normally carried out under atmospheric or superatmospheric pressure, e.g. at a pressure in the range 1 to 100 bars.

65 The source of oxygen may be oxygen itself or oxygen enriched air. The molar ratios of alkane or alkane/alkene mixture and oxygen are preferably in the range 0.1 to 10 moles of oxygen for each mole of alkane or alkane-alkene mixture, for example 0.5 to 2 moles of oxygen for each mole of alkane or alkane/alkene mixture.

70 The source of chlorine is suitably hydrogen chloride or a mixture of chlorine itself and hydrogen chloride, or a mixture of hydrogen chloride and/or chlorine and chlorinated hydrocarbons (e.g. chlorohydrocarbons such as ethyl chloride, ethylene dichloride). It is preferred to use hydrogen chloride or a mixture of chlorine and hydrogen chloride (including ammonium chloride which on heating decomposes to give hydrogen chloride). Typically, the reaction mixture contains 0.1 to 10 moles of hydrogen chloride, for example 1 to 3 moles of hydrogen chloride for each mole of alkane or alkane/alkene mixture.

75 The products of the reaction may be isolated and used as such or, if desired, may be recycled wholly or partially to the reactor in order to increase the yield of monochlorinated olefin, e.g. vinyl chloride.

The invention is illustrated by the following Examples.

EXAMPLE 1

A Cu/Mn/Ti catalyst was prepared as follows: to 170 ml of a 15% solution of titanium tetrachloride was added an equal volume of water, followed by ammonium hydroxide until the pH of the 5 solution was greater than 7.0. The resulting precipitate was filtered and washed until free from chloride. To this precipitate was added a mixture of 6.5 ml of a 50% solution of Mn(NO₃)₂.6 H₂O and 3.62 g of Cu(NO₃)₂.3 H₂O dissolved in 40 ml of water. The resulting mixture was evaporated to dryness, heated at 120°C for 16 hours and finally calcined at 500°C for 16 hours.

After grinding to 250—500 µm mesh size, the catalyst was loaded into a $\frac{1}{4}$ " O.D. tubular micro 10 reactor (equipped with an on-line G.L.C. system) to give a bed length of 5 cm or 10 cm. The catalyst was pretreated in a current of HCl for 1 hour at 400°C followed by N₂ for 15 minutes at 250°C. Catalytic performance was then evaluated under a range of gas feed conditions and over a range of temperatures. The products were analysed using on-line G.L.C. The results obtained are shown in Table 1.

15 The catalyst used in this Example had a Cu : Mn : Ti atomic ratio of 1 : 1 : 10.

15

EXAMPLE 2

A Cu/Mn/Ti catalyst was prepared and tested as in Example 1 but with an atomic ratio of 1 : 1 : 15. The results given in Table 2 were obtained with a feed rate of 25 ml min⁻¹ air, 5 ml min⁻¹ ethane and 5 ml min⁻¹ HCl.

20 EXAMPLE 3

A Cu/Mn/Ti catalyst having an atomic ratio of 1 : 4 : 4 was prepared and tested as in Example 1. Results are summarised in Table 3.

20

TABLE I

TABLE 2

Temp. °C	Conversion %	Selectivity %					
		CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.
400	50.2	6.0	1.4	0.5	20.9	2.9	1.7
450	77.4	6.0	13.5	19.4	0.1	11.1	6.6
475	83.3	5.6	28.0	29.9	2.5	8.1	4.7
500	86.5	6.6	49.5	29.5	0.2	4.6	2.8

TABLE 3

Temp. °C	Conversion %	Selectivity %						β Tri
		CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.	
400	44	16	3.3	1.7	7.2	9.4	6.1	48.8
425	61.8	12.0	8.5	8.8	0.5	15.5	9.4	36.3
450	60.2	17.3	18.8	25.4	—	14.4	8.5	18.0
500	74.1	9.1	44.1	27.2	—	7.6	4.7	4.0

EXAMPLE 4

A Cu/Ce/Th/Mn/Ti catalyst was prepared in the following manner: to 85 ml of a 15% solution of TiCl₄ was added 2.038 g of (NH₄)₂Ce(NO₃)₆ dissolved in 30 ml water and a solution of 2.234 g of Th(NO₃)₄. 6 H₂O in 55 ml water. To the resulting mixture 50 ml of 25% NH₄OH was added to give a pale yellow precipitate which was filtered and washed with water until the washings were no longer alkaline. 5 A mixture of 1.819 g Cu(NO₃)₂.3 H₂O in 40 ml of water and 3.2 ml of a 50% solution of Mn(NO₃)₂.6 H₂O was added to the yellow precipitate and allowed to stand for 16 hours. The mixture was then evaporated to dryness and heated overnight at 120°C. The temperature of the furnace was gradually increased to 500°C, after which the catalyst was calcined for 16 hours at 500°C. The catalytic 10 performance was then evaluated in a microreactor as in Example 1 and the results obtained are shown 10 in Table 4.

The catalyst used in this Example had a Cu:Ce:Th:Mn:Ti atomic ratio of 1:0.5:0.5:1:10.

EXAMPLE 5

A Cu/Me/Fe/Ti catalyst was made in the following manner: a solution of 85 ml of 15% TiCl₄ was 15 mixed with 3.03 g of Fe(NO₃)₃.9 H₂O dissolved in 10 ml water and the resulting mixture diluted with an equal volume of water. A 25% solution of NH₄OH was added (60 ml) to give a yellow-brown precipitate which was then allowed to stand overnight. The precipitate was filtered and washed alkaline-free. To this precipitate was added a mixture of 1.609 g Cu(NO₃)₂.3 H₂O in 40 ml water and 3.2 mol of a 50% 20 solution of Mn(NO₃)₂.6 H₂O. When the addition was complete, the resulting slurry was thoroughly stirred and allowed to stand for 16 hours. The mixture was then evaporated to dryness, dried overnight at 120°C and finally calcined at 500°C for 16 hours. The catalyst was packed into a microreactor and tested as in Example 1. The results obtained are shown in Table 5. 20

TABLE 4

Air	Ethane	HCl	Temp. °C	Conversion %	Selectivity %						
					CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.	E.D.C.
25	5	5	350	26.45	6.35	1.07	0.28	15.31	2.36	1.28	72.44
25	5	5	400	56.62	14.14	17.76	23.97	0	10.59	5.11	26.45
25	5	5	425	71.17	12.73	24.72	33.08	0	10.19	5.02	12.54
25	5	5	400	82.79	7.95	35.31	31.99	0	13.73	4.68	4.77
12.5	2.5	2.5	400	48.16	19.05	12.34	27.17	0	10.88	5.62	22.92
12.5	2.5	2.5	425	58.40	15.11	18.56	36.99	0	10.21	5.23	12.34
12.5	2.5	2.5	425	62.61	12.65	13.92	37.43	0	13.65	7.01	13.61
12.5	2.5	5.0	425	67.76	3.61	8.33	34.58	0	20.98	11.20	19.19
12.5	2.5	6.0	425	36.67	1.82	36.71	32.42	0.21	6.87	3.11	18.39

TABLE 5

Air ml min ⁻¹	Ethane HCl	Temp. °C	Conversion %	Selectivity %				
				CO ₂	C ₂ H ₄	V/C	EC	Cis D.C.E.
25	5	5	350	27.50	10.15	0.97	0.25	17.64
25	5	5	400	53.17	24.22	18.77	16.22	0.08
25	5	5	450	58.33	17.56	28.82	31.44	0.08
25	5	5	500	79.35	8.53	52.63	29.12	0.26

The catalyst used in this Example had a Cu : Mn : Fe : Ti atomic ratio of 1 : 1 : 1 : 10.

EXAMPLE 6

- A Cu/Mn/Zn/Ti catalyst was prepared as follows: a solution of 3.718 g of Zn(NO₃)₂.6 H₂O in 100 ml of water was mixed with 11.3 ml of a 50% solution of TiCl₄. The solution was made ammoniacal by 5 the addition of NH₄OH and the resulting precipitate filtered and washed until alkali-free. To the washed precipitate was added a mixture of 3.02 g Cu(NO₃)₂.3 H₂O in 35 ml water and 5.3 ml of 50% Mn(NO₃)₂.6 H₂O. The mixture was evaporated to dryness, dried for 16 hours at 120°C and finally calcined at 500°C for 16 hours. The catalyst was packed into a microreactor and its catalytic performance evaluated as in Example 1 and the results obtained are shown in Table 6.
- 10 The catalyst used in this Example had a Cu : Mn : Zn : Ti atomic ratio of 1 : 1 : 1 : 8. 10

Notes on Tables 1—7

- VC = vinyl chloride
EC = ethyl chloride
Cis D.C.E. = cis dichloroethylene
15 Trans D.C.E. = trans dichloroethylene 15
EDC = ethylene dichloride
 β Tri = β -trichloroethane

TABLE 6

Air	ml min ⁻¹	Ethane	HCl	Temp. °C	Conversion %	Selectivity %					
						CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.
25	5	5	400	43.02	16.22	3.78	15.62	0.22	23.66	15.05	19.95
25	5	5	425	53.32	17.78	9.95	34.22	0	15.99	9.31	8.00
25	5	5	450	57.29	16.13	19.48	38.35	0.15	13.50	7.88	1.36
25	5	5	475	63.70	12.37	33.29	34.04	0.13	10.29	6.07	0.17
25	5	5	500	73.95	8.85	49.36	27.07	0.03	7.24	4.30	0

EXAMPLE 7

A range of compositions of Cu/Mn/Zn/Ti catalysts were prepared and evaluated as in Example 6. The results of reaction at 450°C are summarised in Table 7.

TABLE 7

Catalyst Comp. (atomic)				Selectivity %									
Cu	Mn	Zn	Ti	Temp. %	Conv. %	CO ₂	C ₂ H ₄	VC	EC	Cis D.C.E.	Trans D.C.E.	E.D.G.	β Tri
1	1	1	1	450	57.6	13.4	1.4	5.5	2.4	15.1	7.4	32.0	7.5
1	1	1	2	450	60.1	12.9	14.6	31.9	—	14.3	7.0	15.1	—
1	1	1	6	450	53.6	18.4	36.5	36.5	—	14.4	8.1	1.2	—
1	1	1	9	450	62.4	13.5	19.9	40.0	0.1	12.5	7.0	4.0	—
1	1	2	25	450	49.0	14.9	6.4	15.9	0.1	26.4	16.0	4.4	—
1	1	2	10	450	82.7	25.4	5.4	16.6	—	22.2	14.1	1.3	5.4
1	2	1	8	450	67.2	21.1	6.7	27.1	—	14.8	10.6	12.2	—

CLAIMS

1. A process for the production of a monochlorinated olefin which comprises bringing into reaction at an elevated temperature a gaseous mixture comprising an alkane, a source of chlorine and molecular oxygen in the presence of a solid particulate catalyst composition comprising compounds of copper, manganese and titanium. 5
2. A process according to claim 1 wherein the catalyst composition also includes one or more compounds of cerium, thorium, iron or zinc.
3. A process according to claim 1 or claim 2 wherein the alkane is ethane.
4. A process according to any one of the preceding claims wherein the catalyst composition is 10 such that the atomic ratio of copper:manganese:titanium is in the range 1:0.1:1 to 1:10:25. 10
5. A process according to claim 4 wherein the atomic ratio of copper:manganese:titanium is substantially 1:1:10.
6. A process according to any one of the preceding claims wherein the gaseous mixture contains from 0.1 to 10 moles of oxygen for each mole of alkane.
- 15 7. A process according to claim 6 wherein the gaseous mixture contains from 0.5 to 2 moles of oxygen for each mole of alkane.
8. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples. 15

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25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.